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Double modulation-high resolution infrared spectroscopic technique: The ν_3 band of the CH_3 radical and excited states of CH_4 in a hollow cathode discharge

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In this work several lines of the ν_3 fundamental band of the CH_3 radical have been detected in a refrigerated hollow cathode discharge multipass cell filled with CH_4 , by using a discharge and laser amplitude double modulation technique, with a difference frequency laser spectrometer and a double phase sensitive detection. Bands of the precursor CH_4 and of C_2H_4 and C_2H_6 produced in the discharge have been observed too. By Doppler broadening and absorption variations, the increase of temperature with the establishment of the discharge has been tested. It is only $\sim 15^\circ\text{C}$. Nevertheless, a very high sensitivity in transmittance variations with temperature is achieved for transitions from highly excited levels of stable species. The method proposed can be very useful for the assignment of very weak bands.

I. INTRODUCTION

The methyl radical is one of the most important intermediates in chemical reactions. Calculations of the molecular evolution of dark clouds in the interstellar medium have shown that CH_3 may be one of the most abundant free radicals.¹ In hydrocarbon combustion, CH_3 recombination may be a key step in the formation of two-carbon species^{2,3} and it has been considered to be the key active species in deposition of various kinds of carbon thin films from a discharge plasma.^{4,5}

The methyl radical is a planar molecule belonging to the D_{3h} point group and optical emission in the visible region is forbidden from its first excited electronic state.⁶ Further Rydberg series, which are all predissociated, have been detected^{7,8} by resonance-enhanced multiphoton ionization (REMPI) spectroscopy. In its electronic ground state, three of its four fundamental vibrational modes have been observed. The out-of-plane bending vibration, ν_2 , was observed by Yamada *et al.*⁹ at 606.4531 cm^{-1} by using a diode laser; Amano *et al.*^{10,11} detected the ν_3 C–H stretching mode fundamental at 3160.821 cm^{-1} with a difference frequency laser spectrometer; and the infrared inactive symmetric stretching frequency, ν_1 , was observed at 3004.8 cm^{-1} by coherent anti-Stokes Raman spectroscopy (CARS).^{12,13} The remaining fundamental frequency, ν_4 , probably lies very close to its Ne matrix value¹⁴ of 1396 cm^{-1} . Because of its symmetry, no rotational transitions in the millimeter or far-infrared region are expected, but the high resolution infrared experiments provide a very accurate description of the rotational structure of the ground electronic state of CH_3 . More limited information is available from the lower resolution CARS spectrum.

Due to its relatively large oscillator strength,^{15,16} the diode-laser infrared spectrum of the ν_2 band has been frequently used for testing the CH_3 role in several photolysis,¹⁷ combustion, and discharge processes,^{18–20} but similar measurements making use of the ν_3 band have not been published since its experimental observation and assignment in 1982.^{10,11} This region, where the vib-rotational

C–H stretching bands appear,^{22,23} is covered without discontinuities by the difference frequency laser system initially developed by Pine²¹ and would be very useful to characterize a major part of the species involved in hydrocarbon processes. Besides, although the ν_3 band would be necessary to detect interstellar CH_3 radicals, making use of the atmospheric window at $3\text{ }\mu\text{m}$, to date not even the transition dipole moment is accurately known, the only datum reported being that of the Ne matrix experiment,¹⁴ which showed that its absorbance was around eight or nine times smaller than that of the ν_2 band. More recently work suggests that it is even weaker.²⁴

The main problem in obtaining the spectrum of a transient species is to distinguish it from the spectra of the parent molecules and other stable products, which are usually present with several orders of magnitude higher concentrations. Several methods have been developed, but none of them seems to be definitively adequate for the methyl radical. This species is one of the more stable hydrocarbon radicals. Its lifetime is a function of its concentration because recombination in the gas phase to give ethane is, besides surface reactions, the main way of disappearance.^{25–27} For this reason the well-known spectroscopic method for the detection of transients based on discharge modulation and phase sensitive detection^{28,29} cannot be used for CH_3 at the appropriate high modulation frequencies, where electrical noise is low. Being a neutral, velocity-modulation laser spectroscopy³⁰ is unsuitable. Moreover, source-frequency modulation can neither be used for the ν_3 band because the lines due to the parent molecules of CH_3 and the reaction products are so congested that the spectrum recorded with this technique looks almost continuous. In Ref. 11, Zeeman modulation was used as the best choice for the observation of the ν_3 band of the paramagnetic CH_3 , among the other much stronger diamagnetic products, in spite of being a very inefficient method, due to the fact that spin-rotation splitting was of the same magnitude than the linewidth.²⁴

In this work a new high resolution spectroscopic

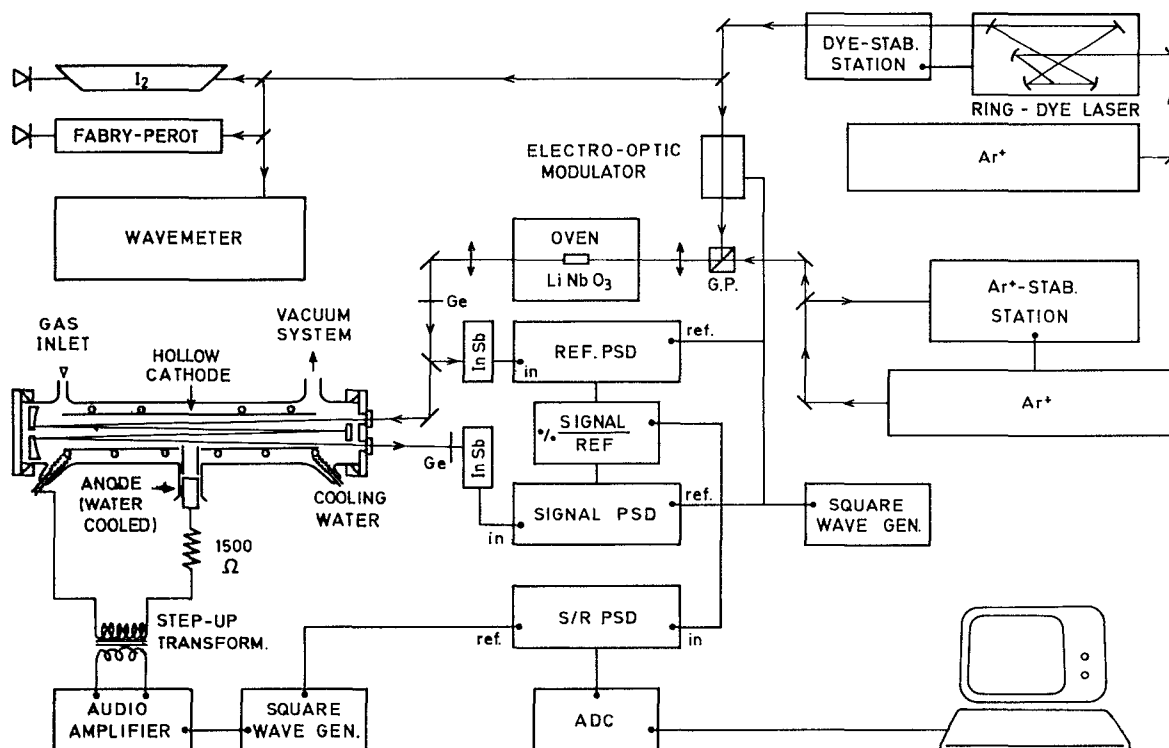


FIG. 1. Schematic diagram of the experimental setup.

method to study the weak ν_3 band of the CH₃ radical is described. It is based on a difference frequency laser spectrometer and a double discharge-laser-amplitude modulation, with a double phase-sensitive detection. In contrast to Zeeman or source frequency modulation techniques, it provides directly the nondispersive profile transmittance spectrum of CH₃, which allows one to obtain easily the dipole moment once its concentration is known. On the other hand, this method allows the observation at the same time, but separately, of the transmittance spectra of stable species involved in the discharge, and can be very useful in order to characterize the whole behavior of this and other very interesting physical systems involving hydrocarbons.

The technique has also proved to be very sensitive to thermal population variations of stable species in the discharge. For highly excited levels, it provides greatly enhanced absorption signals for small changes in temperature, making this spectroscopic method a valuable tool for the assignment of vib-rotational transitions from these levels. As an example, the behavior of several lines of CH₄ has been observed. In fact, for this major air pollutant,^{31,32} increasing $\sim 1\%$ per year due to anthropogenic causes, 9% of transitions are still unidentified³³ in the region around 3000 cm^{-1} , where lines belonging to the ν_1 , ν_3 , $2\nu_2$, $\nu_2 + \nu_4$, and $2\nu_4$ bands of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ (pentad region)^{34,35} mix with the hot bands $\nu_3 + \nu_4 - \nu_4$ and $\nu_2 + \nu_3 - \nu_3$ and with forbidden transitions, and where the theoretical analysis fails to reproduce all the experimental data, particularly at higher J values.

II. EXPERIMENTAL METHOD

The experimental setup used in this work is shown schematically in Fig. 1. The difference-frequency laser spectrometer has been described previously.³⁶ It has been constructed in our laboratory,³⁷ following the design of Pine.²¹ Briefly, the output of a frequency stabilized Ar⁺ laser is mixed collinearly with that of a ring dye laser (Spectra Physics 380-D) and focused into a 5 cm long, a -cut LiNbO₃ crystal, held in a temperature controlled oven (stability better than 0.05°C) to achieve phase matching. About $1\text{ }\mu\text{W}$ of IR radiation, 3 MHz linewidth, is generated at 3000 cm^{-1} from 400 mW Ar⁺ and 80 mW dye laser intensities, linewidth being mainly limited by the dye laser frequency jitter. The wavelength coverage is from 2.2 to $4.2\text{ }\mu\text{m}$, limited by the LiNbO₃ crystal. IR radiation is modulated at high frequency (15 kHz) by means of an electro-optic modulator situated at the output of the dye laser. Two liquid nitrogen refrigerated InSb detectors (Judson IR-JD10), in a dual beam configuration, and two lock-in amplifiers (Stanford Research Systems SR510), synchronized with the electro-optic modulator, are used to obtain the transmittance spectrum. It is given as the ratio between signal and reference outputs, divided analogically for noise reduction purposes. Although the generated IR power is 10^4 – 10^5 times greater than the noise equivalent power of the detectors, in spite of the dual phase sensitive detection and ratio normalization process, the best signal/noise ratio attained in the transmittance spectrum is about

10³ because of interference fringes, dye laser instabilities, and IR beam wandering. A subtraction method³⁸ was proved to be even less efficient in this case.

Usually the I₂ absorption spectrum has been used as frequency standard for the dye laser radiation, which limits the absolute accuracy of the frequency scale of the IR spectrometer to 10⁻³ cm⁻¹, according to the accuracy of the tabulated I₂ wave numbers.³⁹ For a better accuracy, a wavemeter built in our laboratory⁴⁰ has been used in some cases for fixed wavelengths. It has a precision of 5 in 10⁹ and an accuracy of 1 in 10⁸, and operates between 0.4 and 1.1 μm. In other cases, IR lines of C₂H₄ and C₂H₆ appearing in the discharge have been used for the calibration.²² Marks of a Fabry-Perot interferometer allow one to linearize the spectra.

Methyl radical and methane excitation have been obtained with a current modulated, methane hollow cathode discharge,^{29,41} refrigerated by water, in a multipass White cell.⁴² Its construction was based following the design of Van den Heuvel and Dynamus⁴³ and is described elsewhere.^{44,45} The cathode is a copper cylinder, 70 cm long and 5 cm wide. The stainless steel anode is mounted on a side arm, in front of a hole drilled in the midpoint of the cathode. A circular piece cut from a stainless steel sheet 0.1 mm thick is placed on the anode surface and changed each time the cell is cleaned. Good electrical contact between the anode and the sheet is obtained with a conductive paint (Nural 11). This avoids the need of polishing the surface of the anode. A glass tube, inserted between electrodes, prevents occurrence of the discharge outside the cathode. In order to obtain a good pressure distribution of CH₄ in the cell and a more uniform discharge along the cathode, gas was supplied through a glass tube (diameter: 1 cm) with small holes along it, placed inside the cathode.

Efficiency of CH₃ production in the discharge, operating at a modulation frequency of 1.2 kHz, was previously tested by mass spectrometry^{44,45} with a quadrupole, using the threshold ionization technique²⁶ and the difference between the appearance potential of dissociative ionization of CH₄ to give CH₃ (14.3 eV)⁴⁶ and the ionization potential of the free radical CH₃ (9.8 eV).⁴⁷ In that case, given the relatively high modulation frequency, methyl radical concentration was supposed to be approximately constant at the stationary regime, its value being 0.2% of the remaining CH₄, for a 95 mA, 800 V, 2 mbar of pure CH₄ discharge. In the present work a low discharge modulation frequency is essential for the formation and complete disappearance of CH₃ during each modulation period. To obtain it a 1500 V, 150 mA dc source made in our laboratory, feeding a set of transistors activated with a square-wave generator, has been used for frequencies below 50 Hz. An audioamplifier with a set-up transformer has been used for higher frequencies.

The transmittance signal, that is to say, the ratio between absorption and reference signals, with the two lock-in amplifiers operating at their shortest time constants (1 ms), feeds a third lock-in amplifier synchronized at the frequency of the discharge. Its pre- and post-time constants are 1 s. The output of this third lock-in gives directly the

variation in the transmittance spectrum of the cell due to the modulation of the discharge, resulting from the appearance of transient species and from the variation in the level population of the stable species. The amplitude of these modulated signals is usually so small that they cannot be appreciated directly in the transmittance spectrum. Some attempts without laser modulation and a single lock-in synchronized to the frequency of the discharge, similar to those used for other radicals,^{29,48} were unsuccessful in this case, due to the background noise level and the IR laser instabilities, which are both large in comparison to the weak CH₃ signals at the required low discharge modulation frequencies. Endo *et al.*⁴⁹ used double phase sensitive detection for similar reasons, with discharge and source frequency modulation to obtain the diode laser spectrum of the SF radical.

III. RESULTS AND DISCUSSION

A. CH₃ transitions

The goal of this work was not to obtain the complete spectra of CH₃ or CH₄ in the 3000 cm⁻¹ region, but to test the usefulness of the new spectroscopic method and to obtain the transition dipole moment of the ν₃ band of CH₃.⁵⁰ With this method five lines of the ν₃ band of the methyl radical at 3072.913, 3101.042, 3108.798, 3153.324, and 3154.746 cm⁻¹ have been observed until now. Among them, only those at 3153.324 and 3154.746 cm⁻¹ had been observed before.^{10,11} The predicted positions of the other three,⁵¹ with the molecular constants of CH₃ given by Amano *et al.*,¹¹ were 3072.9067, 3101.0400, and 3108.8015 cm⁻¹. Their intensities were estimated to be similar to those of the former two lines at a moderate temperature (around 300 or 400 K), and two or three times stronger than many of the other observed lines reported in Ref. 11, but very close lying lines of C₂H₄ made it difficult to assign them to CH₃ directly. The addition of 1–6 mbar of He produced a gradual decrease of C₂H₄ signals up to their complete disappearance, while the amplitude of CH₃ lines did not change.

Figure 2 is an example of the transmittance spectra and variation of transmittance (third lock-in) spectra in the region around the ⁷Q₀(2) line of CH₃. To obtain these spectra, 1 mbar of pure CH₄ at a 7 l mbar/s gas flow rate has been used in the hollow cathode discharge cell, operating at 64 Hz, 800 V, 45 mA, with an optical path of 8.4 m along the discharge. Previous attempts varying the frequency of the discharge showed a large depletion of the CH₃ signal for values higher than 80 Hz. Transition ⁷Q₀(2) has been selected to be shown here because its corresponding Zeeman spectrum appears in Fig. 2 of the mentioned work of Amano *et al.*¹¹

Figures 2(a) and 2(c) show the spectra with discharge off; Figs. 2(b) and 2(d) have been obtained with discharge on. Figures 2(a) and 2(b) show the transmittance spectra. Without discharge (a), only two peaks belonging to CH₄ appear. They are two R₁₂ forbidden lines of the ν₃ band of CH₄⁵² at 3154.9311 and 3154.8872 cm⁻¹. With discharge on (b), these maxima deplete because of a net decrease in methane concentration, and other transitions belonging to

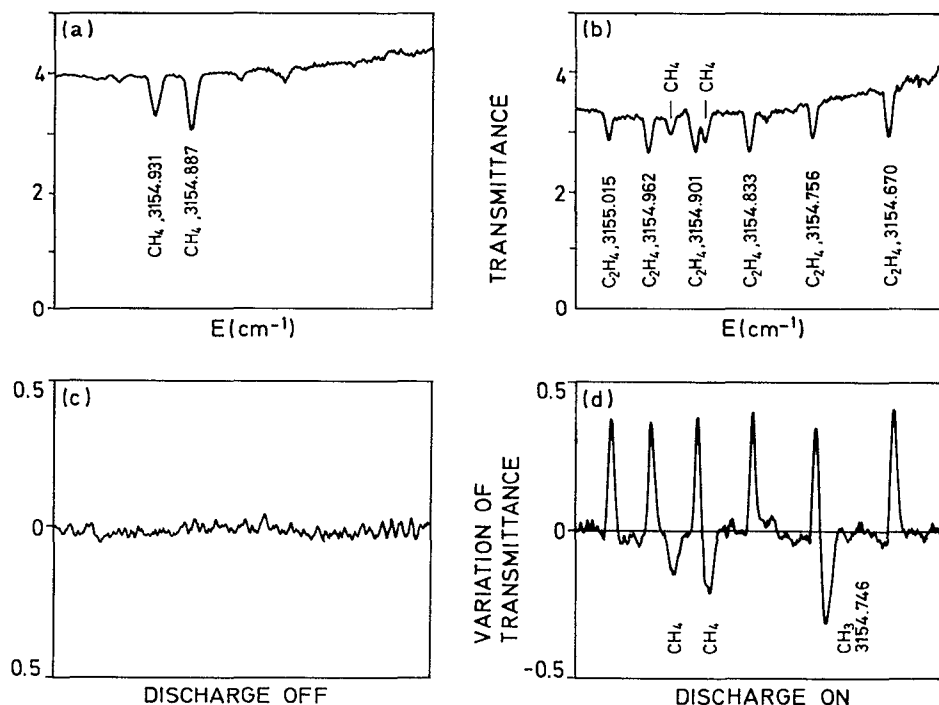


FIG. 2. Example of the spectra obtained in this work in the region around the ${}^{\circ}Q_0(2)$ line of CH₃ at 3154.746 cm⁻¹. Figures on the left show spectra with discharge off; figures on the right have been obtained with discharge on. Upper figures show the transmittance spectra. Lower figures show the variation of transmittance spectra.

the product C₂H₄ appear. In other spectral regions, some C₂H₆ transitions appeared too.²² In Figs. 2(c) and 2(d), the "modulated variation of transmittance" spectra are shown. Spectra 2(c) and 2(d) are amplified 50 times in relation with spectra 2(a) and 2(b), according to the gain scale of the third lock-in. With discharge off Fig. 2(c), only noise is recorded. With discharge on Fig. 2(d) the CH₄ and C₂H₄ transitions observed in the transmittance spectrum 2(b), as well as the ${}^{\circ}Q_0(2)$ line of CH₃ at 3154.746 cm⁻¹, can be seen. Signals of opposite sign appear. The signal due to CH₃ can be explained as a true variation in concentration, as long as [CH₃] follows modulation cycle. Nevertheless positive or negative peaks of the stable species in this spectrum can be assigned, respectively, to a depletion or growth in population of the lower energy level of each transition; this will be explained in more detail below.

From Fig. 2, an absorption coefficient of the ${}^{\circ}Q_0(2)$ CH₃ line $\sim 2.5 \times 10^{-6}$ cm⁻¹ is estimated. For the best signal/noise ratio attainable in the transmittance spectrum, a minimum detectable absorption coefficient of 10^{-7} cm⁻¹ can be inferred.

For the methyl radical, whose population disappears completely within each modulation period, the translational temperature may be evaluated from the Doppler linewidth in the third lock-in spectrum, which in this case is proportional to the absorbance spectrum. The observed mean broadening (FWHM) of 0.0099 ± 0.0008 cm⁻¹, corresponds to an effective temperature of 290 ± 50 K. From the intensity relations among the observed CH₃ lines, a rotational temperature of 300 K ($\pm 10\%$) is inferred.

B. CH₄ transitions

As mentioned in Sec. III A the objective of the discharge and laser amplitude double modulation method was to detect the weak ν_3 transitions of the methyl radical in order to obtain its transition dipole moment, making use of its modulation in concentration at low frequency. As the density of stable species involved in the CH₄ discharge was not supposed to change appreciably during each modulation period at the stationary state, i.e., ~ 15 s after the discharge is turned on, it could be thought that only lines belonging to unstable species would appear in the variation of transmittance spectrum. Nevertheless several lines of CH₄, C₂H₄, and C₂H₆ appeared in this third lock-in spectrum and besides some of them were greatly enhanced in comparison with the conventional transmittance spectrum. As methane is the most abundant of the stable species in the discharge, its spectrum was more exhaustively studied here.

The most enhanced CH₄ lines in the variation of transmittance spectrum were transitions from high energy levels. Transitions from low energy levels showed signals of opposite sign with a smaller relative amplitude. These facts cannot be due to variations of CH₄ concentration and could be explained by a variation of the effective temperature, modulated with the discharge. On the other hand, different line shapes were observed for CH₄ transitions in the third lock-in spectra. These spectra, once converted to variation of population distributions with the aid of the transmittance spectra, ranged from near Gaussian func-

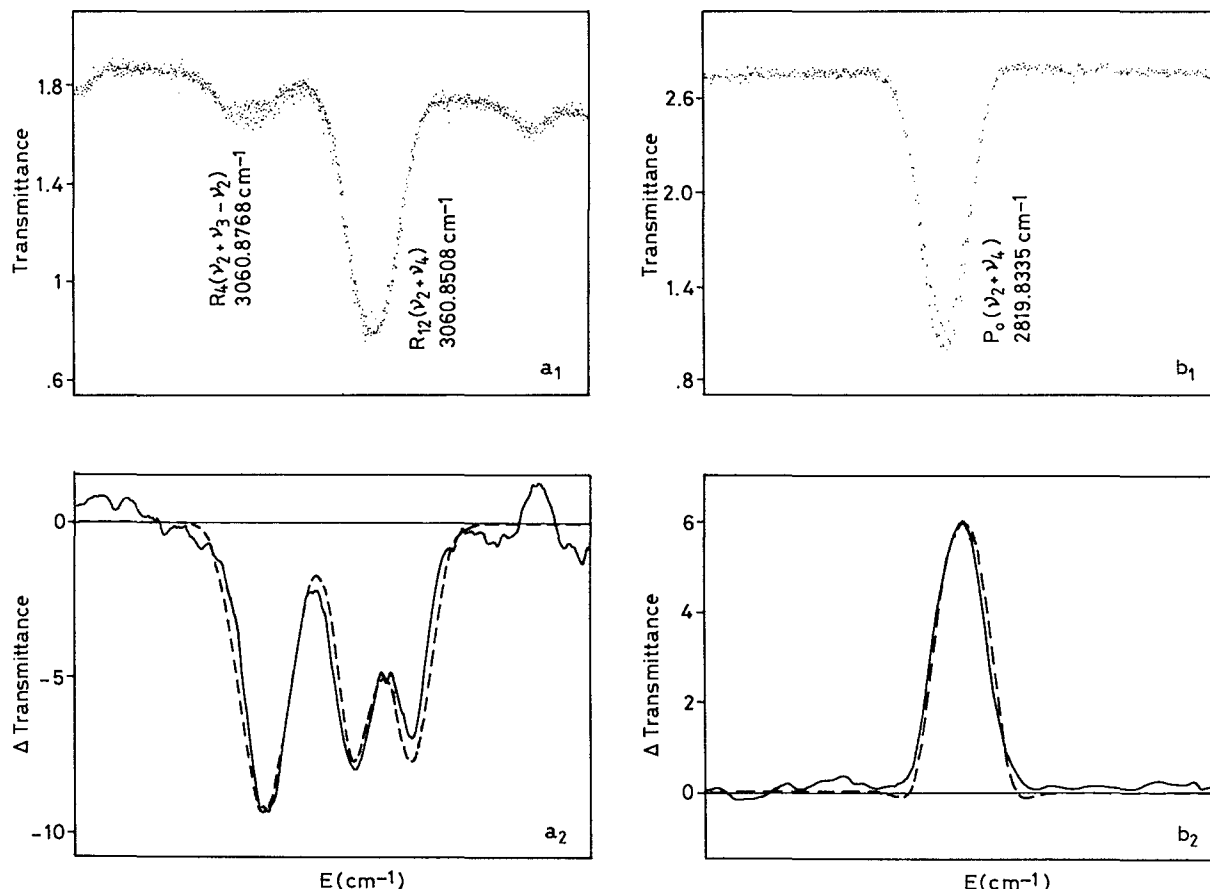


FIG. 3. Transmittance spectra of CH₄ (up) and variation of CH₄ transmittance spectra (down) due to an increase in temperature during the discharge. Three CH₄ lines from very different low energy levels are shown. The broken lines are the best theoretical fits. From these, an increase of $\sim 15^\circ$ above ambient temperature is inferred (see the text).

tions with different linewidths to symmetrical functions with a dip at their line center. All of them could be explained as a difference between two Doppler broadened distributions at two different translational temperatures, their shapes depending on the intensity relation between both curves, which involves vib-rotational temperature variation. Figure 3 shows some representative cases.

Figures 3(a₁) and 3(a₂) show the spectra of the R_4 line ($4, A_2, 1 \rightarrow 5, A_1, 1$) of the hot band $\nu_2 + \nu_3 - \nu_2$ ⁵³ at $3060.8768 \text{ cm}^{-1}$, and the R_{12} line ($12, A_1, 1 \rightarrow 13, A_2, 3$) of the $\nu_2 + \nu_4$ band⁵⁴ at $3060.8508 \text{ cm}^{-1}$, their lower energy levels being at 1640.1239 and 814.6462 cm^{-1} , respectively.⁵⁵ In Figs. 3(b₁) and 3(b₂) is shown the P_1 line ($1, F_1, 1 \rightarrow 0, F_2, 1$) of the $\nu_2 + \nu_4$ band at $2819.8335 \text{ cm}^{-1}$, the energy of its lower level being 10.4815 cm^{-1} . Figures 3(a₁) and 3(b₁) correspond to the transmittance spectra of the discharge, operating at 1 mbar CH₄, 18 Hz, 900 V, 95 mA, for the mentioned lines. Figures 3(a₂) and 3(b₂) are their variation of transmittance spectra. The broken curves are the best fits of the difference between two Gaussian distributions, with different linewidths and amplitudes, to the variations in population experimentally obtained from these spectra. Variations in transmittance are +40%, +10%, and -8% for the lines arising from the energy

levels at 1640 , 814 , and 10 cm^{-1} , respectively. It can be seen how the variation in transmittance strikingly increases with the energy of the lower level, being large enough for the line at $3060.8768 \text{ cm}^{-1}$ of the hot band to be appreciable directly on the transmittance spectrum 3(a₁) as a dispersion of measurements at this peak remarkably higher than that attributed to noise. From linewidths, a mean translational increase of $(14 \pm 3)^\circ \text{C}$ above ambient temperature may be deduced from discharge off to discharge on. From differences in intensities a mean increase in vib-rotational temperature of $(16 \pm 2)^\circ \text{C}$ is inferred.²³ As can be seen, a remarkably high precision in the temperature determination of CH₄ in the discharge is achieved with this method. The mean quadratic error increases slightly (up to $\pm 4^\circ \text{C}$) when spectra of discharges obtained in different days are considered. This may be due to small differences in the discharge conditions. Similar results are obtained for ethylene produced in the discharge. They coincide very well with CH₃ results. From these data the low increase in temperature of neutral species attained with the hollow cathode discharge can be noticed.

The assignment of transitions of stable species arising from levels of high energy is usually achieved by obtaining, in a neutral medium, their transmittance spectra at two

very different temperatures.⁵⁴ Alternatively, a few results have been reported for microwave spectroscopy by using rf discharges of continuous amplitude in order to increase the population of excited levels.^{56,57} In both cases, very weak lines may be buried in noise or overlapped with more intense transitions, and variations in their absorbance due to temperature variation may be hardly noticeable.

Being a "zero method," the detection of phase sensitive transmittance variations with a modulated discharge provides, even for very small changes in the effective temperature, an enhanced sensitivity, large enough to detect transitions from highly excited levels, which often are not observable in the conventional transmittance spectrum. Figure 4 shows an example of this fact. Figure 4(a) is the transmittance spectrum around 3109 cm⁻¹ of 1 mbar of CH₄ with an optical path length of 16 m. Figure 4(b) is the variation of transmittance spectrum of the discharge. One line of the methyl radical at 3108.798 cm⁻¹ appears in this region; all the remaining lines belong to methane. Lines at 3109.064, 3109.122, and 3109.304 cm⁻¹ are three R_8 forbidden transitions of the ν_3 band.⁵² The energy of their lower levels is close to 376 cm⁻¹. Lines at 3108.712, 3108.675, and 3108.493 cm⁻¹ are R_{10} transitions of the $\nu_3 + \nu_4 - \nu_4$ hot band.⁵⁸ The energies of their lower energy levels are 1827.3975, 1827.2918, and 1826.8843 cm⁻¹, respectively. Being very weak in the transmittance spectrum 4(a), transitions of the hot band provide a very large signal in transmittance variation with the modulated discharge. Conversely, transitions from the ν_3 band, with much larger absorption coefficients but involving lower energy levels, provide small signals in Fig. 4(b) spectrum. More striking is the case of the lines at 3109.166 and 3109.206 cm⁻¹. To our knowledge, they still remain unidentified. They are so weak that 10 mbar of CH₄ and 12 m of optical path (with the resultant saturations of the most intense lines) have been needed to detect them in the transmittance spectrum 4(c). Nevertheless they can be seen clearly in Fig. 4(b). From Fig. 4(c) line strengths of 1.8×10^{-4} cm⁻² atm⁻¹ for both lines are obtained. Taking into account Figs. 4(a) and 4(b), this implies variations in transmittance of 40% and 35%, respectively, with the discharge. Then, for an increment in temperature from 300 to 318 ± 3 K as deduced in this spectrum from the other lines, and from a spherical top molecule rotational partition function, lower energy levels of these transitions with values 1700 and 1530 cm⁻¹ ($\pm 25\%$) may be inferred. The line at 3108.974 cm⁻¹, which can be seen in Fig. 4(c) is a R_8 transition of the ν_3 band; the energy of its lower level is 373.82 cm⁻¹. Being that its absorbance is relatively weak and that the energy of its lower level is not high, it cannot be seen in Fig. 4(b). One line at 3108.909 cm⁻¹ remains unidentified. As it is not seen in Fig. 4(b) it may be thought that the energy of its lower level is small. In a similar way CH₄ transitions in the spectral regions around the CH₃ lines reported here have been examined and several unassigned transitions of CH₄ have been found. Some of them, that had not been observed before, have been identified according to Champion's predictions.⁵⁹ This is the case of the lines at 3072.7349 ($Q_{11}(2\nu_2)$), 3100.7798 ($Q_{13}(2\nu_2)$),

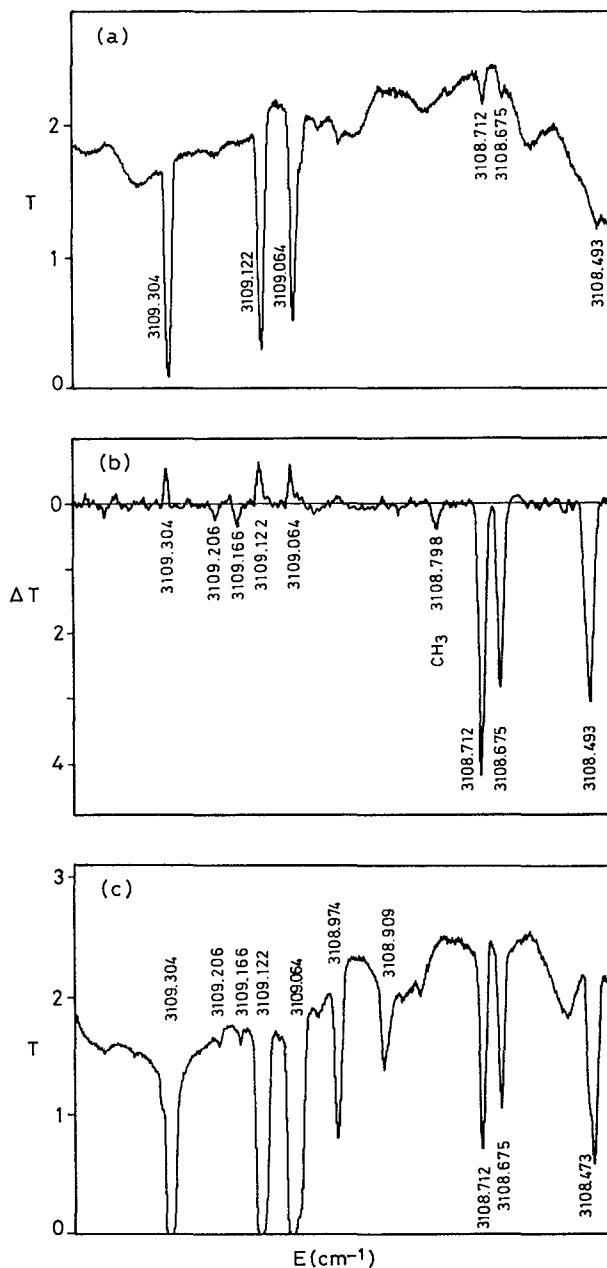


FIG. 4. Significant example of the enhanced sensitivity of the double modulation method to detect transitions from highly excited levels. (a) and (b) are transmittance T and variation of transmittance ΔT spectra obtained with 1 mbar of CH₄ in the multipass cell. ΔT signals of three lines from departure levels of high energy (~ 1827 cm⁻¹), at the right-hand side of the figure, are remarkably higher than these for transitions from departure levels of low energy (~ 376 cm⁻¹), at the left-hand side. Even more, 10 times higher CH₄ pressure is necessary (c) to appreciate in the T spectrum two very weak lines which can be seen in the ΔT spectrum at 3109.166 and 3109.206 cm⁻¹.

3100.7278 ($Q_{11}(2\nu_2)$), and 3153.5125 cm⁻¹ ($R_{19}(2\nu_4)$). A more systematic work employing this technique seems very promising in order to complete the whole assignment of the CH₄ spectrum in this region.

C. CH₄ transients

As was said before, it is known that methyl radical disappearance has long decay times; thus, a low modula-

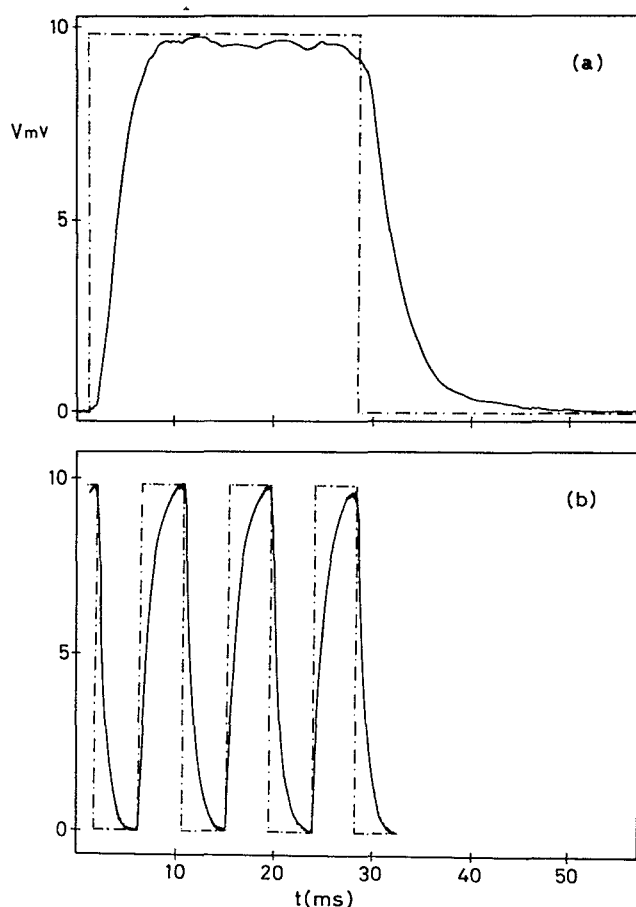


FIG. 5. (a) Temporal evolution of methane energy levels population during one discharge modulation period. (b) Instrumental time response to a square wave modulation signal.

tion frequency of the discharge is necessary to modulate efficiently its concentration. In a similar way, the knowledge of the temporal evolution of the population of CH₄ excited levels at short term is necessary in order to evaluate whether this double modulation method may be extended or not to higher discharge frequencies. Therefore, once equilibrium in the stationary concentrations of stable species was attained, that is to say ~ 15 s after the initial turn on of the discharge, the temporal evolution of CH₄ lines was observed during the whole discharge modulation period. CH₃ transients have been studied also and will be published elsewhere.⁵⁰ To carry out the present study, the transmittance signal, as given by the ratio between signal and reference lock-in outputs, which is usually collected by the third lock in, has been analyzed with a Tektronix 2430A digital oscilloscope working in the average mode. An external high pass filter, $RC=1$ s, removed the dc current. Figure 5(a) is the modulated variation in transmittance of the $\nu_2+\nu_4$ band P_0 line at 2819.833 cm^{-1} . Lock ins 1 and 2 time constants are 1 ms. Instrumental time response of the whole system is represented in Fig. 5(b). It has been obtained with a mechanical chopper, placed just before the signal detector, where the IR beam is focused. From this figure, it can be roughly estimated that the CH₄

(1, F_1 ,1) effective lifetime is ~ 3 ms. Transient analysis of transitions from other vib-rotational excited levels show similar results. The following justifies this result.

Hilico *et al.*,⁵⁶ working with a methane rf discharge at ambient temperature, estimated that the lifetime of excited CH₄ levels was limited by wall deactivation, since the diffusion time from the axis to the wall of the cell, where the excitation was destroyed, was one order of magnitude smaller than the collisional deactivation time for the 110 mTorr of CH₄ used in their work (diffusion time ~ 0.6 ms, collisional deactivation time ~ 12 ms, at 300 K). In our case the geometry and dimensions of the discharge, but not the pressure, are very similar to theirs. Let us see how CH₄ pressure changes these values.

To estimate the diffusion time τ_d , assuming that the walls represent a net sink for the diffusing particles, Fick's law

$$dn/dt = D \cdot \nabla^2 n$$

implies⁶⁰

$$\tau_d = L^2/D,$$

where D is the diffusion coefficient, inversely proportional to pressure,⁶⁰ and L the cell fundamental mode diffusion length. For a circular cylinder of length h and radius r , L is given by the equation⁶¹

$$1/L^2 = (\pi/h)^2 + (2.405/r)^2$$

so a value of $L^2 \sim 1.1\text{ cm}^2$ for the hollow cathode used in the discharge cell is deduced. For 1 mbar of pure CH₄ a diffusion time of 4.5 ms is obtained. Nevertheless, for a correct estimation of τ_d we should take into account that a great part of CH₄ disappears in the discharge. Considering the difference in absorbance signals of the CH₄ lines between discharge off and discharge on, once it is stabilized (i.e., once a transient time ~ 15 s after the discharge is turned on has elapsed), we can assume that up to 70% of methane is destroyed. Then, neglecting the contribution to CH₄ diffusion from other species appearing in the discharge, τ_d would decrease up to ~ 1.4 ms.

In relation with collisional deactivation time, it is known that all electronically excited states of CH₄ are of the Rydberg type and are unstable, their potential surfaces lying above the lowest dissociation limit.⁶² Rotational excitation transfer can be characterized by a single, very small rotational collision number ($Z_r=12$ for CH₄ at 300 K),⁶³ which implies a rotational relaxation time, $\tau_r=1\text{ }\mu\text{s}$ for 1 mbar of CH₄, very small in comparison with the time scale of the experiment. So relaxation from excited vibrational levels should be the key process of the whole collisional deactivation of CH₄ in the gas phase. Although vibrational relaxation among upper levels and the $\nu_4=1$ level is fast,⁶³ methane shows the highest collision number for vibration-translation energy transfer^{63,64} among polyatomic molecules containing more than two hydrogen atoms ($Z_v=15160$ at 300 K). From this value a collisional deactivation time ~ 2 ms would be inferred here if 1 mbar of pure CH₄ were considered. Nevertheless, as relaxation time is inversely proportional to pressure, a value of 4.6 ms

would result for a 70% decrease of CH₄ in the discharge. As can be seen, although diffusion and relaxation decays follow opposite behavior with pressure, in this case they have very similar values. Within the uncertainty of the methane concentration during the discharge and the effect of other species, the values placed between their upper and lower limits agree with the population decay of CH₄ levels experimentally observed. Then it may be assumed that both processes can be responsible for the temporal variation of transmittance in the discharge. From these results it may be deduced that for the physical condition and the cell dimensions considered here, modulation frequencies of CH₄ discharges below ~200 Hz are suitable to apply this method for the assignment of highly excited levels. For other species with faster decays, the highest frequency of operation may be limited by the lower available instrumental time constants.

IV. CONCLUSIONS

In this work a new double-modulation, high resolution spectroscopic method, giving nondispersive line shapes, is reported. It proves to be very sensitive to detect long lived transient species. With it some new lines of the weak ν_3 band of the methyl radical have been observed.

The method provides a powerful tool to detect population variations with temperature of very weak transitions from highly excited levels of CH₄ and other stable species produced in the discharge. Its application may help very significantly to their spectroscopic assignment.

Using this method the temperature characterization of several neutral species involved in the hollow cathode discharge has been tested and remarkably low temperatures have been obtained. An extension of this spectroscopic method to microwave or radio-frequency discharges, extensively used for different physical processes, seems possible with a low frequency amplitude modulation of their electrical power sources.

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